

## FTIR spectroscopic and thermal studies of calcium tartrate trihydrate crystals grown by gel assistance

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**Abstract** : Single crystals of calcium tartrate trihydrate were grown by using silica gel as a medium. The gel was set by acidification of sodium metasilicate solution by orthophosphoric acid solution. The supernatant solution containing calcium chloride and tartaric acid was poured on the gel. However, this is in contrast to the usual growth technique for growing calcium tartrate crystals, where the gel is set with tartaric acid and calcium chloride is used as a supernatant solution. The crystal growth and the role played by gel is discussed. The crystals were characterized by FTIR spectroscopic technique and thermogravimetric analysis. A kinetics of dehydration was studied by using the Coast-Redfern, the Horowitz-Metzger and the Freeman – Carroll Relations.

**Keywords** : Gel growth, FTIR spectroscopy, calcium tartrate trihydrate, crystal

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### 1. Introduction

As tartrates are sparingly soluble in water and decompose before melting, the gel growth technique is found to be more promising than the high temperature crystal growths. Calcium tartrate crystals are found to be exhibiting ferroelectric and non linear optical properties [1-5]. The ferroelectricity in gel grown calcium tartrate was reported by Gon [4]. Many authors have reported gel growth of calcium tartrate [6-9] and mixed strontium-calcium tartrate crystals [10, 11]. Recently, Suryanarayana *et al.* [5] have studied optical and structural characteristics of strontium doped calcium tartrate as well as Suryanarayana and Dharmaprakash [12] have reported defect characterization of the same crystals. The growth of pure and mixed calcium and strontium tartrate crystals using optically active dextro tartaric acid [13] and levo tartaric acid [14] have also been carried out.

The present investigation is a part of the detail study carried out to grow calcium hydrogen phosphate crystals by diffusing calcium chloride solution into the gel impregnated by orthophosphoric acid, which yielded platelet and needle-shaped calcium hydrogen phosphate crystals. When tartaric acid was

added along with the calcium chloride in the supernatant solution instead of calcium hydrogen phosphate, the crystals of calcium tartrate grew in the gel. These crystals were characterised by FTIR spectroscopic and thermogravimetry techniques.

### 2. Experimental techniques

Glass test tubes of 2.5 cm diameter and 15 cm length were used as a crystal growth apparatus. The gel was set by acidification of sodium metasilicate solution of specific gravity 1.06 by orthophosphoric acid of 2.5 molarity. After setting the gel, the supernatant solution containing 10 ml calcium chloride and 10 ml of 1 molar tartaric acid was gently poured without disturbing the gel.

Transparent crystals with prismatic faces were grown at the liquid-gel interface and inside the gel. The growth of crystals is shown in Figure 1. The largest crystal having dimensions of 8 mm × 7 mm × 3 mm was harvested, which is shown in Figure 2.

Whether the direct reaction took place or not between calcium chloride and tartaric acid solutions in the absence of gel medium, was also verified. In a single test tube of the same dimension, a mixture of tartaric acid solution and calcium chloride

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solution was poured and kept for 3 weeks under the identical conditions, but no crystal growth was observed. This process was repeated by adding orthophosphoric acid, which also did not yield any crystal growth. It was found that the role of gel in crystal growth was important.

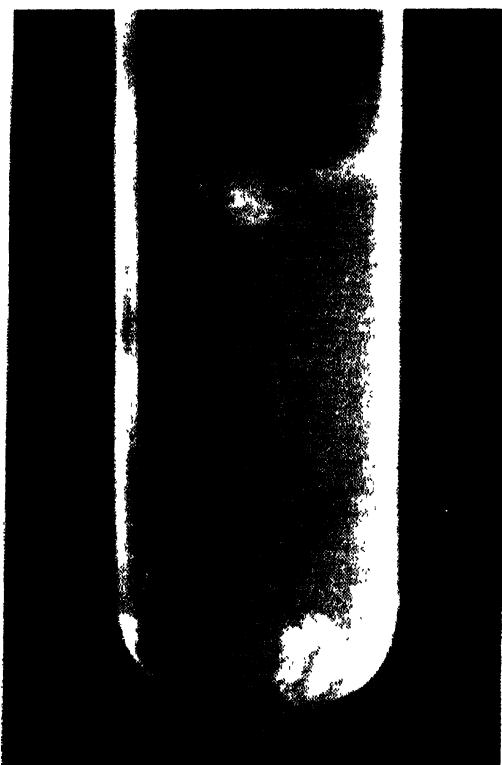


Figure 1. The growth of calcium tartrate crystals in test tube



Figure 2. The largest calcium tartrate crystal harvested.

The Fourier transform infrared (FTIR) spectrum of the powdered samples in KBr medium was recorded in the region from  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  by BRUKER IFS 66V FTIR spectrometer. The thermogram of the crystal was obtained with the help of STA 409C set up. Thermogravimetric analysis (TGA) was performed from room temperature to  $1000^\circ\text{C}$  at heating rate of  $15^\circ\text{C}/\text{min}$  in the atmosphere of nitrogen by using alumina as reference material. Powdered samples were used.

### 3. Results and discussion

Ambady [15] studied the crystal structure of calcium tartrate tetrahydrate crystals. The crystals were found to be orthorhombic with  $a = 9.24 \pm 0.02\text{ \AA}$ ,  $b = 10.63 \pm 0.02\text{ \AA}$  and  $c = 9.66 \pm 0.02\text{ \AA}$  having space group  $P 2_1 2_1 2_1$ . Recently Suryanarayana *et al* [5] reported crystal structure of strontium doped calcium tartrate crystals.

For the growth of calcium tartrate, it is customary to diffuse  $\text{CaCl}_2$  from a solution into the silica gel charged with tartaric acid, which has been described in detail by Henisch [7]. However it has been possible to pre-supersaturate the growth medium with calcium tartrate by adding a small amount of  $\text{CaCl}_2$  before the gel sets. Due to subsequent calcium chloride diffusion from the supernatant solution, a very large number of small crystals uniformly distributed in gel are found. When the gel is not pre-saturated, the normal highly nonuniform distribution of crystals is expected, which indicates that the number of crystals reduces on going away from gel-solution interface. It has also been found that the crystals which grow at substantial depths in the gel grow more slowly than those near the top because of the smaller concentration gradients.

In cases involving the salts of weak acids, the environment becomes increasingly acidic during growth, and the likelihood of a nucleus reaching critical size is correspondingly reduced. Halberstadt and Henisch [8, 9] have shown that calcium tartrate does not readily nucleate at pH values less than 3. Higher perfection at increasing depths is due to reduced competition. However, by adding HCl to the  $\text{CaCl}_2$  solution, fewer and better quality crystals have been produced nearer to the gel interface.

Gels are neither liquid nor solid, it is not a simple three dimensional network, actually it consists of sheet-like structure of varying degrees of surface roughness and porosity, forming interconnected cells. The cell walls are ordinarily curved. In dense gels, the pores are from  $0.1\text{ }\mu\text{m}$  to  $0.5\text{ }\mu\text{m}$ , whereas in low density gel, those are from less than  $0.1\text{ }\mu\text{m}$  to  $4\text{ }\mu\text{m}$ . At some stage in gel, as the concentration of the diffusant increases, a few nuclei begin to form. It is also believed that these act as sinks and result in the establishment of radial patterns which actually reduce reagent concentration in some of neighbouring sites consequently additional nuclei would be inhibited. Subsequent increase of reagent concentration increases the growth rate of new nucleations. An additional reduction of nucleation is also possible by 'natural' suppressive action of the gel. Generally homogeneous nuclei of critical size cannot form in very small

isolated pores because the required amount of solute is not available. Critical nuclei may form in larger pores, however, they are not expected to grow to macroscopic size unless there is enough connection with other pores bearing solute. This is also applied to heterogeneous nuclei. Some of these might be completely 'protected' by gel matter and thus be inoperative, while others might happen to be in suitable locations in which continued growth can be supported by the diffusion condition prevailing. Henisch [7] has discussed this elaborately and suggested that there are favourable and unfavourable pore size distributions.

So far the majority of workers [6-9] have used calcium chloride as supernatant solution to diffuse into silica gel impregnated by tartaric acid; nevertheless, in the present work the gel was set by orthophosphoric acid and calcium chloride and tartaric acid solutions were allowed to diffuse in to gel. As there was no growth of crystals observed by direct reaction between calcium chloride and tartaric acid solutions, it is believed that during diffusion of solutions in gel some critical nuclei might have been formed at suitable pores and might have obtained solute from neighboring pores through the proper channels. If these pores were at gel-liquid interface, the nuclei might get solute directly. It was observed in the present investigations that some good quality crystals were grown at the gel-liquid interface into liquid side as well as in the gel up to the bottom of test tube. This can be seen from Figure 1. It was also observed, when tartaric acid was not added to the calcium chloride containing supernatant solution the crystals of calcium hydrogen phosphate were grown; on the other hand, the addition of tartaric acid completely inhibited the growth of calcium hydrogen phosphate and only crystals of calcium tartrate were grown. The critical nuclei of calcium tartrate seemed to be formed more readily than calcium hydrogen phosphate and the growth of calcium hydrogen phosphate was completely inhibited.

Infrared spectroscopy is one of the powerful technique to identify certain chemical groups and bonds in the sample [16]. The FTIR spectrum of the powdered sample is shown in Figure 3. The absorptions at  $3558\text{ cm}^{-1}$ ,  $3423\text{ cm}^{-1}$  and  $3277\text{ cm}^{-1}$  are attributed to the asymmetric and symmetric stretching of O-H bond, which usually indicates the presence of water of crystallization. The absorption at  $1589\text{ cm}^{-1}$  is due to carbonyl C

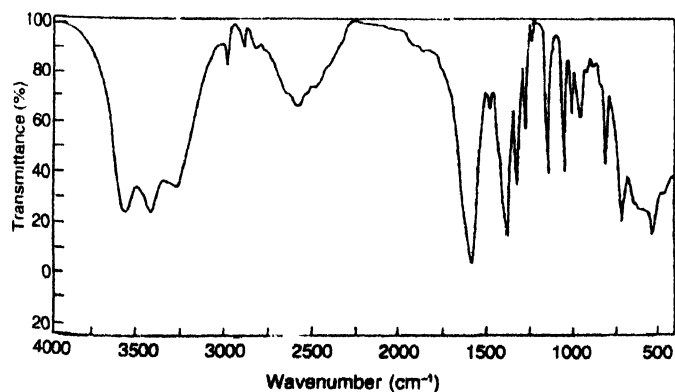


Figure 3. The FTIR Spectrum of calcium tartrate.

= O group. The C-O stretching vibrations give rise to absorptions at  $1488\text{ cm}^{-1}$ ,  $1330\text{ cm}^{-1}$  and more sharp at  $1385\text{ cm}^{-1}$ . Also, the absorptions at  $1061\text{ cm}^{-1}$  and  $1011\text{ cm}^{-1}$  are due to out of plane O-H deformation and C-O stretching. The absorptions situated between  $962\text{ cm}^{-1}$  to  $533\text{ cm}^{-1}$  are due to calcium-oxygen stretching vibrations. However, the mechanical stiffness constant is also calculated for C = O vibration at  $1589\text{ cm}^{-1}$  by using the following relation [16] which is found to be  $1020\text{ Nm}^{-1}$ .

$$\bar{\nu} = 1303(F(1/m_1 + 1/m_2))^{1/2}$$

where  $F$  = force constant in  $\text{Nm}^{-1}$ ,  $m_1 = 16\text{ a.m.u.}$ ,  $m_2 = 12\text{ a.m.u.}$ ,  $\bar{\nu}$  = stretching vibration.

The thermal properties of the gel grown calcium tartrate crystals grown by using dextro-tartaric acid [13] and levo-tartaric acid [14] have been reported. In the present investigation, thermogravimetric analysis (TGA) was carried out on powdered samples. Figure 4 indicates the thermogram of calcium tartrate. It can be noticed that the sample loses water of hydration and becomes anhydrous at  $231^\circ\text{C}$ , thereafter, it decomposes into calcium oxalate, further decomposition into calcium carbonate occurs at  $507^\circ\text{C}$ . Ultimately, the sample turns into calcium oxide at  $835^\circ\text{C}$  and remains stable upto the end of the analysis. It was estimated that three water molecules were associated with the crystals.

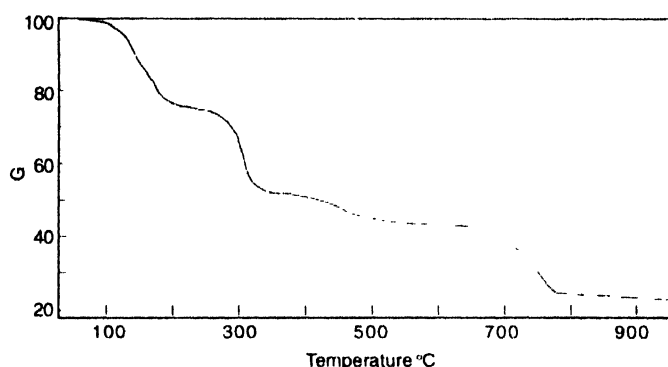


Figure 4. The thermogram of calcium tartrate

The use of thermogravimetric data to evaluate the kinetic parameters of solid state reactions involving weight-loss has been investigated by many workers [17-21]. Usually, the shape of pyrolysis curve is determined by the kinetic parameters such as the order of reaction, the frequency factor and the activation energy. Joseph and Joshi [20] reported the kinetic study of dehydration of gel grown iron tartrate dihydrate crystals. They applied the Coats-Redfern relation, the Horowitz-Metzger relation and the Freeman-Carroll relation to compute various kinetic parameters. The same three relations are applied to the present investigations, hence the details are avoided.

Figure 5 is a plot for the Coats-Redfern relation, which exhibits a linear nature for the value of  $n$ , the order of reaction, to be  $3/2$ . The values of activation energy, frequency factor and entropy were estimated to be  $68.92\text{ kJmol}^{-1}$ ,  $5.43 \times 10^{19}$  and  $131.07$

$\text{JK}^{-1}\text{mol}^{-1}$ , respectively. These values are comparable to the values of calcium levo-tartrate trihydrate crystals [14], but the difference is quite large for calcium dextro-tartrate monohydrate

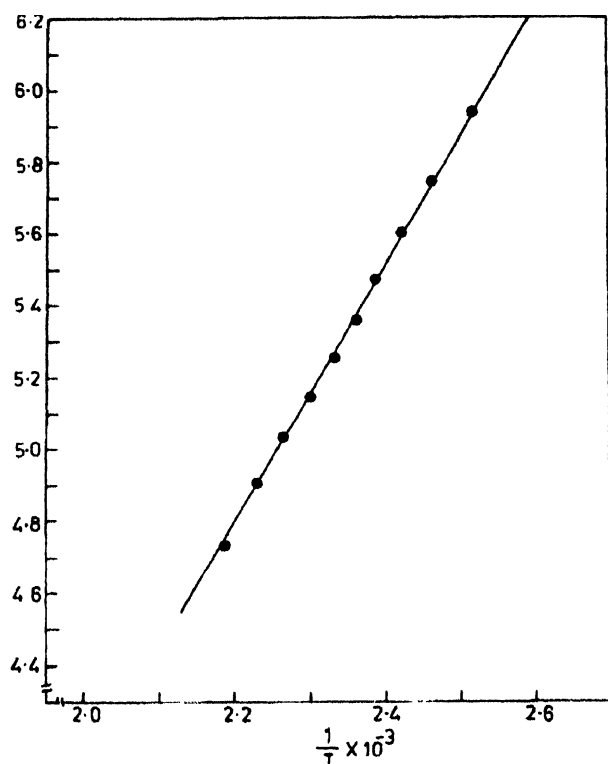


Figure 5. A plot for Coats-Redfern relation, where  $Y = -\log [(1-(1-\alpha)^n)/(1-n)T^2]$  versus  $X = 1/T$ .

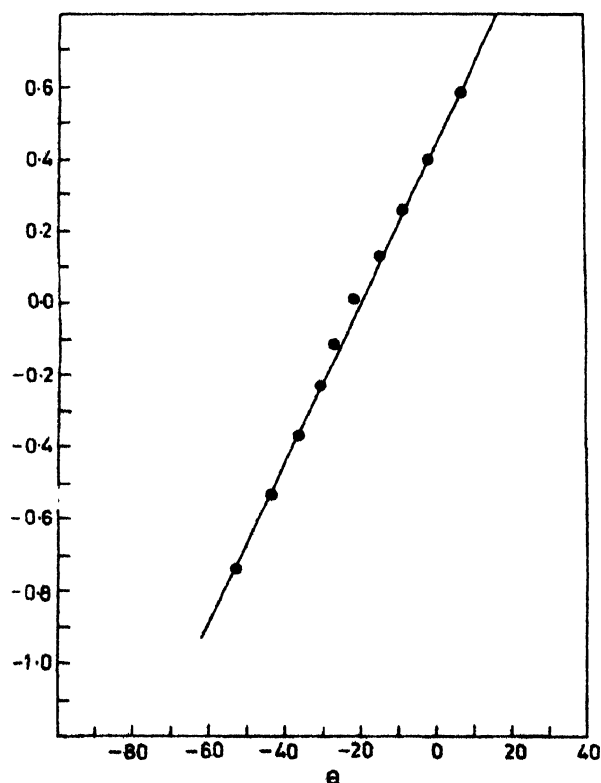


Figure 6. A plot for Horowitz-Metzger relation, where  $Y = \log [(1-C)^n/(1-n)]$  and  $X = \theta$ .

crystals [13]. The Horowitz-Metzger relation plot is shown in Figure 6, which is a linear plot for the value of  $n = 3/2$ . The value of activation energy was calculated to be  $77.20 \text{ kJmol}^{-1}$ . Figure 7 shows the Freeman-Carroll relation, which is again a linear

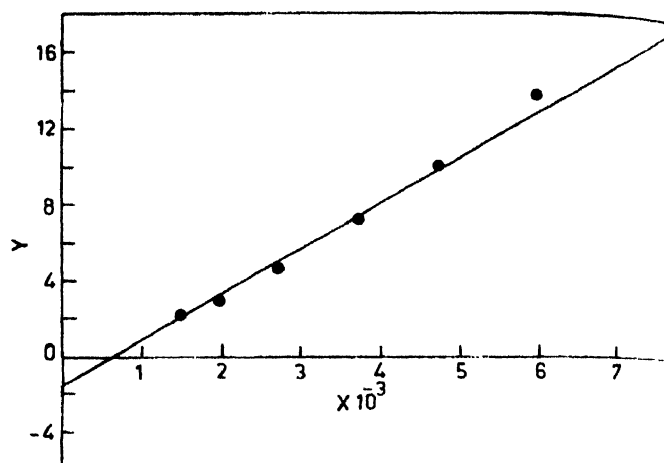


Figure 7. A plot for Freeman-Carroll relation, where  $Y = (\Delta \log dw/dw)/(\Delta \log W_r)$  and  $X = (\Delta T^{-1})/(\Delta \log W_r)$ .

plot for  $n = 3/2$ . The value of activation energy was found to be  $45.95 \text{ kJmol}^{-1}$ . The results are summarized in Table 1. The values of activation energy are found to be different in these relations due to different mathematical treatments applied to explain the mechanism of decomposition, which corresponds to earlier results [20, 21]. The FTIR and TGA results have confirmed the growth of calcium tartrate crystals. Also it was observed that under certain conditions some single crystals were found to be floating on the supernatant liquid surface. Further work is under progress.

Table 1. Shows the values of kinetic parameters calculated for three different relations.

Relation	Order of Reaction	Activation Energy $E$ $\text{kJmol}^{-1}$	Frequency Factor	Entropy $\text{JK}^{-1} \text{mol}^{-1}$
Coats-Redfern	3/2	68.92	$5.93 \times 10^{19}$	131.07
Horowitz-Metzger	3/2	77.20	—	—
Freeman-Carroll	3/2	45.95	—	—

#### 4. Conclusions

Though the crystal growth by direct reaction between calcium chloride and tartaric acid solutions is not observed, the growth is possible in a gel as well as at the gel-liquid interface by pouring simultaneously both the solutions on a gel impregnated by orthophosphoric acid. This may be due to the formation of critical nuclei in suitable pores in the gel and the supply of solute from neighbouring pores through proper channels. The pores bearing nuclei at the gel-liquid interface obtain solute quite readily.

The addition of tartaric acid solution to calcium chloride solution in the supernatant solution has inhibited the growth of calcium hydrogen phosphate completely ; as a result, only the growth of calcium tartrate is observed.

The FTIR spectrum of calcium tartrate trihydrate has revealed the presence of O–H bond, C–O and carbonyl C = O bond. The presence of water molecules are detected.

From the thermogram, it is indicated that the calcium tartrate trihydrate crystals are thermally unstable and decompose into calcium oxide through many stages. The values of kinetic parameters in the relations viz, Coats-Redfern, Horowitz-Metzger and Freeman-Carroll relations, are different for different relations because different mathematical treatments applied in these models. The FTIR and TGA results further confirm the growth of calcium tartrate trihydrate crystals.

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